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Residues of Chlorpyrifos and Its Pyridinol Metabolite in Apples, on Twig Bark, and in Undertree Debris

Abstract

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When chlorpyrifos (Lorsban 4E) was applied to apple trees at the rate of 12 to 15 kg/ha for control of climbing cutworms and San Jose scale, residues were higher in undertree debris (297.2 ppm) than in the fruit (<0.005 ppm) or on the bark (0.19-1.19 ppm) at harvesttime. At harvest, residues were found in the fruit after either one or two applications of the insecticide at higher rates (24 to 30 kg/ha). The amounts of the pyridinol metabolite recovered indicate that chlorpyrifos was lost from debris in summer primarily by volatilization and in winter by hydrolysis. On bark and fruit, degradation was more by hydrolysis. Chlorpyrifos (Lorsban 4E) gave good control of both climbing cutworms and San Jose scale in apple orchards.

KEYWORDS: chlorpyrifos, Lorsban 4E, insecticide residues, apples, cutworms.

Residues of Chlorpyrifos and its Pyridinol Metabolite in Apples, on Twig Bark, and in Undertree Debris[1]

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Introduction

Field tests have shown that chlorpyrifos (Lorsban® 4E) effectively controls the spotted cutworm, Amathes c-nigrum (L.) (Howell and George 1979), bertha armyworm, Mamestra configurata Walker (Howell and Anthon 1977), San Jose scale, Quadraspidiotus perniciosus (Comstock) (Howell 1979), and peach tree borer, Synanthedon exitiosa (Say) (Anonymous 1981) in apple orchards in eastern Washington. Chlorpyrifos is also toxic to codling moth, Cydia pomonella (L.) (MacQuillan 1976, Zénon-Roland et al. 1976). These reports indicate that chlorpyrifos has potential for use in orchard pest management programs, unless its persistence has an adverse impact. Therefore, we expanded a previous study (Howell and George 1979) to determine if chlorpyrifos from 1977 treatments persisted on debris into the 1978 season. In some studies (Brady et al. 1980), chlorpyrifos was more persistent on inert and decaying organic material or in soil (Davis and Kuhr 1976) than on living tissue. Undertree debris were rich in decaying organic material, which would enhance the residual life of chlorpyrifos. Considering the high residues in undertree debris in the fall, carryover to the next season would be possible.

Full tree sprays of chlorpyrifos have been used to control San Jose scale on bark (Howell 1979). Because chlorpyrifos was especially persistent on the bark of pine trees (Brady et al. 1980), we needed to determine if residues were equally persistent on apple tree bark. If so, then the potential for extended control of San Jose scale was high. Brady found 14 to 18 percent of the original deposit of chlorpyrifos still remaining on the bark 15 months after treatment.

We also needed to determine if either t
ground cover sprays or full tree sp
on the harvested fruit

Material and Methods

Chlorpyrifos (Lorsba
(4.67 to 5.61 kl/ha)
35.15 kg/cm^2 at rate
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trees, grown in a Ritzville silt loam soil (coarse-silty mixed mesic calciorthidic Haploxeroll), were used for these experiments. In one test, full cover sprays were applied April 25, 1978. On July 10, half the trees were treated again. The test was a completely randomized design with single tree replicates, 10 replicates per treatment for 'Red Delicious' and seven for 'Golden Delicious'. Ten twigs, ½-1 cm in diameter, 10 cm long, were collected on July 6 and October 4 and 50 apples per tree were collected at harvest (Sept. 26) for residue analysis. All twig and fruit samples were frozen until processed for analysis.

In another test (Howell and George 1979), an area of undertree debris 2 m in diameter was sprayed for control of climbing cutworm and for residue analysis. The undertree debris were primarily dry plant material--that is, mixed leaves from the tree, orchard- and Bermudagrass, Canada thistle, lambs-quarter, mallow, clover, and red-root pig weed. The experimental design was a randomized complete block with four replicates per treatment and four trees per replicate. The untreated control was similarly replicated. Plots were divided so that one set received three applications of chlorpyrifos (April 15, July 13, Aug. 24, 1977), another set two applications (July 13, Aug. 24), and a third set one application (Aug. 24). The orchard was furrow irrigated at 10 day intervals. Samples of debris for residue analysis were collected at apple harvest (Sept. 8) and the following year in spring prebloom (April 18). Each sample consisted of 200 g of debris collected within one-half m radius of the tree trunk. The debris were frozen until processed for residue analysis. Fruit samples were taken from the lower parts of the trees, 10 fruit per tree, at harvest (Sept. 9). The fruit were diced and frozen until processed for analysis.

Residues were determined by the procedure of Howell and George (1979). Recoveries for chlorpyrifos and its metabolite respectively, averaged 90.0 and 103.0 percent in debris, 95.6 and 87.2 percent in fruit, and 96.7 and 104.7 percent on twigs. The sensitivity of the method was 0.005 ppm for both chloryprifos and its metabolite.

Results and in Discussion

Residues of chlorpyrifos and its pyridinol metabolite found in undertree debris and in the fruit when only undertree debris were treated are given in table 1. The undertree debris residue at harvesttime ranged from 350 ppm to 1,735 ppm, depending on the rate and number of applications. However, after overwintering, the residue had decreased to 19

to 172 ppm. When only undertree debris were treated, no residues were detected in the harvested apples.

Chlorpyrifos (Lorsban 4E), when used as a tree spray at the rate of 12 to 15 kg ai/ha was just detectable in the fruit at harvest. However, at the rate(s) of 24 to 30 kg ai/ha, residues were over tolerance on the 'Golden Delecious' variety (table 2), provided that one application was made in July. Residues were essentially nondetectable in fruit at harvest using 25-30 kg ai/ha if the application was in April, in the delayed-dormant stage of bud development (Table 2). When using Lorsban 4E at the rates used here, sprays in July or later would likely result in above tolerance residues.

Getzin (1981) recovered 100 percent of the chlorpyrifos initially applied to peat moss and soil. If, assuming the undertree debris had adsorbed 100 percent, or 1,200 ppm (at 1.2 g ai/L), of the initial deposit, we found that 75 percent of the original deposit had dissipated 15 days after treatment (Howell and George 1979). The same percentage loss was observed on fruit (Zenon-Roland et al. 1976) when the fruit was sampled 14 days after treatment. This finding suggests that the chlorpyrifos residue loss from both fruit and debris are at the same rate from the standpoint of percentage loss. Therefore, our data indicate chlorpyrifos would not have greater stability or persistence on debris than on fruit or twigs. With the major difference being the amount adsorbed onto each substrate, debris (which have more surface area than twig bark) adsorbed more than fruit or twigs.

Other examples where large amounts of chlorpyrifos were adsorbed included peat moss (Getzin 1981) and loblolly pine bark (Brady et al. 1980). However, there are numerous examples similar to twigs where living plant tissue adsorbed only small amounts of chlorpyrifos. These include turf at 68 ppm (Kuhr and Tashiro 1978), mint hay at 258 ppm (Inman et al. 1981), wheat plants at 30 ppm (Struble and McDonald 1973), bermudagrass at 12 ppm and corn at 8 ppm (Leuck et al. 1975), and pears at 6 ppm and apples at 5 ppm (Zenon-Roland et al. 1976).

Getzin (1981) found that chlorpyrifos was lost from peat moss by volatilization, and that only minimal amounts of the pyridinol metabolite were formed. He also found that in mineral soil, a clay catalyzed hydrolysis converted a large percentage (76 to 94 percent) of the chlorpyrifos to the pyridinol metabolite. Metabolite recoveries in September, in

debris, were <1 percent of the chlorpyrifos recovered (table 1); but in April the average was 13.1 percent (table 1). On twigs, the metabolite averaged 9.2 percent; on 'Red' and 'Golden Delicious' apples it was 16.6 and 3.8 percent respectively. In a separate study, we found about 1 to 2 percent pyridinol metabolite on peaches 24 hr postapplication. These data indicate that a high percentage of the chlorpyrifos lost from undertree debris during summer was by volatilization, unless the pyridinol metabolite was further broken down or conjugated.

Overwinter degradation between harvest and blossom dates continues at approximately the same rate as in summer. However, the mechanism of degradation may have changed. Degradation was more by hydrolysis, with an average metabolite level of 13.1 percent (table 1). In summer, the degradation on the bark and fruit involved hydrolysis, based on metabolite residues ranging from 0.46 to 19.46 percent or an average of 9.8 percent (table 2). The lack of hydrolysis of chlorpyrifos on debris during summer may be the reason why there are such high residues on this material.

Chlorpyrifos is a better stomach poison than a contact poison (Cheng 1973). Although many insects are poisoned by small amounts of chlorpyrifos, such as 0.08 to 2.27 ppm for crickets (Harris 1977) or 3 to 8 ppm for stored grain pests (Lahue 1977), other insects required high doses, such as over 400 ppm for cutworm larvae (Ascher and Nemny 1977; Howell and George 1979) and 893 ppm for the southern pine beetle (Brady et al. 1980). Therefore, the high residues found in the undertree debris would be toxic to the sensitive fauna there, unless the residues are tightly adsorbed or modified to become nontoxic.

In conclusion, our data show cutworms can be controlled by treating only undertree debris and that this treatment will not leave overtolerance residue on the fruit at harvesttime.

Table 1. Residues of chlorpyrifos and its metabolite (trichloro-2-pyridinol) on apple orchard undertree debris, Yakima, Wash., at harvest and after overwintering

Rate (g ai/L)	Spray dates in 1977	Number of applications	Residues found (ppm)[1]			
			September 1977[2]		April 1978	
			Chlorpyrifos	Metabolite	Chlorpyrifos	Metabolite
1.2	Aug. 24	1	[3]297.2 (±81)	1.1 (±1.1)	19.7 (±6)	1.4 (±0.6)
	July 13, Aug. 24	2	500.6 (±154)	2.0 (±0.7)	39.3 (±8)	5.1 (±1.8)
	Apr. 15, July 13, Aug. 24	3	350.5 (±126)	2.7 (±1.2)	51.1 (±7)	6.9 (±2.7)
2.4	Aug. 24	1	1011.2 (±21)	9.5 (±3.2)	19.3 (±4)	3.7 (±0.1)
	July 13, Aug. 24	2	1436.2 (±312)	6.4 (±2.5)	51.3 (±3)	7.9 (±2.3)
	Apr. 15, July 13, Aug. 24	3	1735.7 (±708)	4.5 (±0.6)	171.9 (±18)	18.6 (±0.5)

[1]Results have been corrected for average recovery from samples fortified with known amounts of chlorpyrifos.

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		Sampling date	Residues found (ppm)[1]			
			'Red Delicious' twigs		'Golden Delicious' twigs	
			Chlorpyrifos	Metabolite	Chlorpyrifos	Metabolite
		July 6, 1978	1.19	[4]<0.005	0.64	0.01
		Oct. 4, 1978	.09	<.005	.19	.02
			.75	.06	1.15	.26
		July 6, 1978	6.02	.23	1.87	.07
			--	--	1.90	.08
	1	Oct. 4, 1978	.19	.01	.22	.04
	2		.98	.08	1.49	.29
			'Red Delicious' apple		'Golden Delicious' apple	
1.2	1	Sept. 26, 1978	<.005	<.005	<0.005	<0.005
	2		.03	<.005	0.09	<0.005
2.4	1		<.005	<.005	<0.005	ND
	2		.03	<.005	0.24	ND

[1]Residues have been corrected for average recovery found.
[2]Treatment date was April 25, 1978.
[3]Treatment dates were April 25 and July 10, 1978.
[4]Minimum sensitivity of the method.

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